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(54) OUTSIDE SITE PRETREATMENT OF CATALYST FOR TREATING HYDROCARBON

(57)Abstract:

**PROBLEM TO BE SOLVED:** To enhance activation of a catalyst in pretreatment of the catalyst outside of a site by introducing a sulfurizing agent into the catalyst, treating the catalyst with hydrogen within a specified temperature range and passivating the catalyst. **SOLUTION:** At least one sulfurizing agent is incorporated in a catalyst, e.g. its pores, outside of a site. This sulfurizing agent is a sulfur compound containing sulfur element, and a molecule containing sulfur can be decomposed under action of hydrogen and produces, particularly, hydrogen sulfide. Under pure hydrogen or diluted hydrogen, the catalyst is treated at 150-700°C outside of the site. In this process, a large flexibility is available in selection level of operation conditions. By this method, an excellent uniformity is realized in distribution of the sulfurizing agent in a catalyst bed. Further, passivation, e.g. oxidation passivation, is to be executed outside of the site and, by this process, an activity higher than that observed in another catalyst having the sulfurizing agent introduced therein is imparted to the catalyst.

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**CLAIMS**

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[Claim(s)]

[Claim 1]A preliminary treatment method characterized by comprising the following outside the spot of a catalyst.

- Introduce a sulphidizing agent into a catalyst.
- catalyst is passivated [ processing a catalyst from hydrogen at 150-700 \*\*, ].

[Claim 2]A method characterized by comprising the following by claim 1.

- Incorporate at least one sulphidizing agent out of the spot into a catalyst at temperature of 0-200 \*\* under existence of at least one ingredient including a carbon to carbon bond of at least one solvent and/or an olefin type.

Scavenging of a catalyst is performed out of the spot with a gas containing processing a catalyst incorporating a sulphidizing agent out of the spot at 150-700 \*\* by purity or dilution-water matter, - air, or oxygen.

[Claim 3]a. Under existence of at least one ingredient including a carbon to carbon bond of at least one solvent and/or an olefin type, . Incorporate at least one sulphidizing agent at 30-200 \*\* out of the spot into a catalyst. b. Under existence of c. purity which performs heat treatment of the bottom of absent of hydrogen and a catalyst out of the spot, or dilution-water matter, e. which processes a catalyst out of the spot at 150-700 \*\* and which cools a catalyst to d. ordinary temperature and neglects this catalyst subsequently to the bottom of inert gas flow -- a method by claim 1 or 2 of performing dilution oxygen lower than about 10% of concentration, and scavenging of a catalyst subsequently according to air out of the spot first (expressed as oxygen capacity).

[Claim 4]A method according [ the first two processes of processing by a sulphidizing agent and hydrogen ] simultaneously to \*\*\*\* claim 1 to break.

[Claim 5]A method by any 1 paragraph of claims 1-4 that a sulphidizing agent is chosen from a group which consists of a sulfur element, organic polysulfide, hydrogen sulfide, mercaptan, carbon bisulfide, a sulfide, disulfide, and a thiophene compound.

[Claim 6]A method by claim 5 that a sulphidizing agent is chosen from a group which consists

of a sulfur element, organic polysulfide, a dimethylsulfide, and dimethyldisulfide.

[Claim 7]A way by any 1 paragraph of claims 2-6 a solvent is white spirit.

[Claim 8]A way by any 1 paragraph of claims 2-6 ingredients are olefin hydrocarbon and an oil which originates in fatty acid especially.

[Claim 9](A sulphidizing agent was incorporated) A method by any 1 paragraph of claims 1-8 of processing a catalyst out of the spot by purity or dilution-water matter at temperature of 250-600 \*\*.

[Claim 10]Use by hydrogen treatment of a catalyst processed by any 1 paragraph of claims 1-9.

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[Translation done.]

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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention]This invention relates to the preliminary treatment method or activation method of the catalyst for hydrocarbon hydroconversion which includes preliminary sulfuration out of the spot of a catalyst first. However, under hydrogen, instead of being activated directly, before being activated (ex situ) and conveying a catalyst subsequently out of the spot under existence of hydrogen, it is again given to air and, subsequently to in the reactor for hydrocarbon conversion, it always fills up with it out of the spot within the reactor for hydrocarbon conversion.

[0002]Therefore, this invention should give incorporating : in performing conditioning of a catalyst by the method of containing the following out of the spot, i.e., - sulphidizing agent, into a catalyst, processing a catalyst by hydrogen at 150-700 \*\*, and - catalyst to air.

[0003]the catalyst by this invention -- for example, an alumina type, the activated alumina support, at least one metallic oxide, or oxidation metalloid (magnesium oxide.) Silica, silica alumina, silica oxidation magnesium, clay, charcoal, or the mixture of these ingredients may comprise an another carrier used as a base, and these carriers, at least a part may show noncrystalline morphology or a crystalline substance gestalt (zeolite) -- further -- a catalyst -- the -- other metal chosen from the fellows who comprise VI and 0.2 to 40% of at least one active metal of a group VIII or cobalt, molybdenum, nickel, and tungsten is included. Generally, it comprises two sorts of these metal, and combines, for example, one of the combination of cobalt molybdenum, nickel molybdenum, and nickel tungsten is used. the [ therefore, / which is a platinum group depending on the case ] -- VIII fellows' precious metals, i.e., platinum, palladium, etc. are used, and it gets.

**[0004]**

[Description of the Prior Art]Therefore, before being used, generally a new article or a regenerated catalyst is given to the sulfuration (preliminary sulfuration) carried out within the reactor for hydrogen treatment by conventional technology. It becomes possible to be included in a catalyst by this sulfuration, the amount of chemicals theories, for example, about 50 to 110% of sulfur, which were calculated about the amount of sulfides of formula (responding to

existing metal)  $\text{Co}_9\text{S}_8$ ,  $\text{MoS}_2$ ,  $\text{WS}_2$ , and nickel $_3\text{S}_2$ . To be sure, the activity phase of this catalyst is a mixed sulfide that these new articles or regenerated catalysts contain the oxide. [0005]In conventional technology, this sulfuration (preliminary sulfuration), It carries out using the temperature near the reaction temperature chosen, or the mixture of a sulfur compound which is an elevated temperature (elevated temperature, more specially than therefore, 180 \*\* temperature of not less than 250 \*\*) more, and was generally diluted in hydrogen for several hours about hydrodesulfurization, hydrocracking, and a hydrogenation reaction. [0006]Now, reproduction of the catalyst is gradually performed under the vendor of catalyst regeneration sometimes disconnected from the industrial device. By the way, it seems that it is rational to consider to return the product which was ready for use to a refiner's origin. This is European Patent EP-B-130 of these people. 850 and EP-B-181 By the effective method of 254, become possible and there, A sulfur compound is incorporated into a catalyst, and behind, this sulfur compound causes sulfuration of a catalyst, or preliminary sulfuration, when [ of a reaction zone (processing zone of a brewing raw material) or a reaction zone ] a catalyst contacts hydrogen immediately in the neighborhood. Naturally, the nest of said sulfur compound may be carried out by the neighborhood or the pan of an industrial device in the disposal plant place of a catalyst according to a request. Similarly, how to incorporate said sulfur compound may be enforced to this new article or a regenerated catalyst out of the spot, before a catalyst is used within an industrial device.

[0007]Subsequently, a refiner or other users of all the, In order to make sulfur and the contained metal react, and in order to make refining of hydrocarbon or conversion reaction start immediately by pouring of the brewing raw material for processing, This catalyst is activated within the reactor for hydrocarbon conversion under existence of hydrogen (for example (as opposed to for example, the catalyst for desulfurization), the temperature of 250-350 \*\*).

[0008]

[Problem(s) to be Solved by the Invention]This method of this invention makes it possible to improve activation of a catalyst, and it is characterized processing of the catalyst under existence of hydrogen and in the outside of the spot, and by attaching a catalyst under air, in order to continue and to perform oxidation passivation of a catalyst. Subsequently, a catalyst is conveyed in this stage at a refiner's origin. This sulfidization is carried out about a new article or a regenerated catalyst.

[0009]

[Means for Solving the Problem]Therefore, in : about a way this invention consists of the following process, i.e., a. catalyst, For example, it is in incorporating at least one sulphidizing agent out of the spot into the porosity, This \*\* A sulfur element (indicated to EP-B 130 850 and 181 254), and organic polysulfide, Hydrogen sulfide ( $\text{H}_2\text{S}$ ), mercaptan, carbon bisulfide ( $\text{CS}_2$ ), Are a sulfur compound chosen from a group which consists of all the molecules of others containing a sulfide, disulfide, a thiophene compound, or sulfur, and a molecule containing this sulfur, It can decompose under an operation of hydrogen and especially hydrogen sulfide is

generated (sulfur, organic polysulfide, a dimethylsulfide (DMS), and dimethyldisulfide (DMDS) are chosen preferably). At least one solvent, for example, white spirit, dearomatization gasoline or gasoline that is not dearomatized, and/or other at least one suitable solvents of all the, At least one ingredient which includes a carbon to carbon bond of an olefin type specially, for example, EP-A-564, An ingredient which is indicated to 317 may be used. As an example, a compound or 99.9 to 0.1 % of the weight of ingredients of 0.1 to 99.9 % of the weight of white spirit or an equivalent solvent, and an olefin type, A mixture which contains said at least one compound or 2 to 98 % of the weight of ingredients of 2 to 98 % of the weight of white spirit or an equivalent solvent, and an olefin type preferably may be used. Said ingredients which are independent or are generally used by mixing may be arbitrary hydrocarbon fractions which may include hydrocarbon or a double bond. This is a petroleum fraction like a fraction produced from an olefin (a monoolefin, diolefin, or polyolefine) or some oil-refining methods especially like a visbreaking, a caulking, and steam cracking which may contain an olefin. It is a triglyceride type of desirable unsaturated fatty acid [ like vegetable oil ] in which this ingredient is also.

[0010]When said compound or an ingredient is chosen from an ingredient of vegetable oil, this compound or an ingredient especially belongs to triglyceride fellows of fatty acid. As an oil, divide and Ethylene acid, for example, myristoleic acid, palmitoleic acid, An oil originating in oleic acid, elaidic acid (geometric isomer of oleic acid), gadoleic acid, erucic acid, and unsaturated fatty acid like polyethylene acid (polyethylene acid, for example, linolic acid, and linolenic acid of an oil) is mentioned. These oils may also contain butanoic acid, caproic acid, caprylic acid, capric acid, lauric acid, myristic acid, pulmitic acid, stearic acid, and saturated fatty acid like arachin acid again, for example. Therefore, an ingredient included in combination of a mixture (mixture-solvent), Have 6-24 carbon atoms, and one piece, two pieces, or fatty acid ester it has three pieces. [ whether combination of an olefin type can be used as a base, and ] Or let animal fatty oil which is oleum rapae, peanut oil, soybean oil, corn oil, sunflower seed oil, safflower oil, palm oil, linseed oil, tallow, or lard be a base. As mentioned above, desirable oils are oleum rapae, peanut oil, soybean oil, corn oil, sunflower seed oil, safflower oil, palm oil, and linseed oil.

[0011]Introduction of a sulphidizing agent is performed, for example in a 0-200 °C temperature requirement. (Further 30-200 °C.)

Therefore, according to the above-mentioned selected temperature, a sulphidizing agent to fusion and/or sublimation, the dissolution, or a pan with a gestalt of suspension. or according to one of the art of the above [ passing a sulphidizing agent by the gaseous phase, or a part ], a part is introduced into a catalyst according to one with the another above-mentioned art. This sulphidizing agent may be introduced under [ of a solvent or other additive agents ] absent.

[0012]b. It consists of being an elevated temperature from 100 °C generally about heat treatment of a catalyst out of the bottom of absent of hydrogen, and the spot, and carrying out at an elevated temperature from 120 °C preferably depending on the case. In a certain case, this processing is especially recommended, when contacting a catalyst, a sulphidizing agent, and a fluid that contains white spirit type a solvent or a family solvent, and an olefin type

compound depending on the case. Therefore, in one side, in order to remove a solvent, an obtained mixture is given to heat treatment in another side, in order to especially trigger a ligation reaction of sulfur and a double bond of an olefin compound. Heat treatment is an elevated temperature from 100 \*\*, and is preferably performed at an elevated temperature from 120 \*\*. Therefore, when a sulphidizing agent is a sulfur element, selectively or on the whole, this sulphidizing agent is combined with a gestalt of polysulfide. This reaction is similar with a reaction in a technical field of tire industry called a publicly known vulcanization operation by other technical fields of all the. This vulcanization operation is used in order to improve mechanical properties of crude rubber, it adds a sulfur element to crude rubber, and then heat-treats. Sulfur reacts to a double bond of crude rubber which is the polyisoprene in which mono- \*\*\*\* forms a crosslinking bond of polysulfide between chains.

[0013]c. 150-700 \*\* consists of processing a catalyst at 250-600 \*\* preferably under purity or dilution (hydrogen [ of 1 to 50% ], further 2 to 20% of dilution) hydrogen, and out of the spot (general -- the bottom of atmospheric pressure, and several hours (for example, 1 to 10 hours) -- the object for intercropping is carried out). In this process, big pliability is used in a selection level of an operating condition. Selection of selection of this operating condition, i.e., temperature, gaseous selection, selection of the degree of dilution, Are selection of character (the fixed bed, a rotation (tournant) floor, a moving bed, an expansion (expanse) floor, a boil (bouillonnant) floor, and a fluid bed) of a catalyst bed, and by selection of this operating condition. Here, good homogeneity in distribution of a sulphidizing agent in a catalyst bed becomes possible with perfect constant temperature to the whole particle of a floor further. This process (c) Process (a) And (b) It may carry out behind. This process (c) Process (a) It may carry out simultaneously, namely, introduction of a sulphidizing agent and processing under hydrogen are performed simultaneously. In this case, process (b) It does not exist.

[0014]d. it consists of cooling a catalyst to ordinary temperature general -- out of the spot, for example under inert gas flow depending on the case, and consists of subsequently to the bottom of a cover of inactive gas (for example, nitrogen) neglecting this catalyst.

[0015]e. It consists of passivating out of the spot. this passivation is oxidation passivation as an example -- desirable -- dilution oxygen (less than 30%, less than 10 more%, and less than 5 more% of capacity concentration) -- and/or, it is in performing scavenging of a catalyst by scavenging air (give the atmosphere) of air. Partial reoxidation of metallic sulfide incorporated throughout one or more processes and into a catalyst is performed (oxidation passivation). Adsorption of oxygen by a catalyst exists throughout this process. Activity higher than activity observed with other catalysts into which a sulphidizing agent was introduced in accordance with a method of advanced technology by this process is given to a catalyst. Consider it as illustration, for example, subsequently 5% and an oxygen density are made to increase by gradually 1%, and contact with a catalyst and dilution oxygen, or all the gases, for example, oxygen molecules, containing oxygen, is quick, or is performed a little in between, and it deals in it.

[0016]Especially this invention is suitable for incorporating a sulphidizing agent into a catalyst for hydrogen treatment, and it is a case where fill up with this catalyst for hydrogen treatment in

a reactor within a zone for hydrogen treatment, and it is again attached within this zone for hydrogen treatment subsequently to the bottom of hydrogen.

[0017]A catalyst which finished processing in which especially other advantages of this method are as follows is ready for use. In refining or petrochemistry, it is usable in this catalyst after an easy start method. This start is low temperature about a brewing raw material for processing, and there is in pouring in directly without completely being further accompanied by danger of extraction of sulfur at a room temperature. A chemically fundamental difference discriminable by analysis of a catalyst exists. That is, one or more sulfide phases exist at the time of an end of hydrogen treatment. That is, when an active element of a catalyst is molybdenum of one or more sulfides, tungsten, cobalt, or nickel, for example. A  $\text{MoS}_2$

(therefore,  $\text{Mo}^{4+}$  is equivalent to one sulfide here),  $\text{Co}_9\text{S}_8$ ,  $\text{WS}_2$ , and nickel $_3\text{S}_2$  type phase exists.

[0018]In this invention and this stage of preparation, a "sulfide" phase in a processed catalyst formed after processing by  $\text{H}_2$  is identified clearly, and is identified by X-ray photoelectron spectroscopy (SPX), and it deals in it. By this method, the oxidation number of molybdenum or tungsten is completely 6 (it  $\text{MoO}_3$  and) at a new article or a regenerated catalyst, for example.

As opposed to being  $\text{WO}_3$ , the oxidation number being mostly (> 50%) 6 further with a catalyst by a method of advanced technology by which preliminary sulfuration was carried out, and the latter catalyst containing an oxysulfide type phase, It is proved that the oxidation number is mainly (generally not less than 70%) 4 ( $\text{MoS}_2$  and  $\text{WS}_2$  type), and it deals in molybdenum or tungsten.

[0019]The very great notional difference between this invention and a method of advanced technology is as follows. That is, a user filled up a reactor with a catalyst for hydrogen treatment containing metal before. This metal is in an oxide state or an oxysulfide state chemically. Still this metal was not activity catalytically and it is only in a reactor that a sulfide was manufactured. This difficult process is a generation process of an activity phase, and having controlled thoroughly was impossible, it cannot adjust it rather than anything, and is not characterized. The purpose of this invention is to carry out direct supply of the activity already catalyst to a user, and before filling up a reactor with the catalytic activity of this catalyst, it can be characterized. All dangers of making catalytic activity into what is not best within a reactor by this invention are removed.

[0020]process (a) quantity of sulfur incorporated into a catalyst in between is what is generally equivalent to 50 to 150% of the required amount of chemicals theories to preliminary sulfuration of an active element of a catalyst -- desirable -- this amount of chemicals theories -- it is more specially equivalent to 90 to 105% 80 to 110%.

[0021]On the other hand, for example by passivation by oxidation, it becomes possible similarly to remove a spontaneous combustion tendency of these sulfuration phases, therefore an easy transfer of a solid within a metallic drum or a container of other molds is attained.

[0022]On the other hand, oxidation passivation is \*\*\*\*\* about an effect positive to catalytic



activity.

[0023]

[Embodiment of the Invention]The following example illustrates this invention. That is, a comparative example illustrates some reserve sulfurizing methods of the advanced technology with activation of a catalyst under hydrogen in the spot in the reactor for hydrocarbon conversion. Although the example by this invention illustrates the same reserve sulfurizing method as the advanced technology, before it conveys this catalyst subsequently to in the reactor for hydrocarbon conversion with activation of the catalyst under hydrogen and in the outside of the spot according to this invention, it always illustrates the reserve sulfurizing method accompanied by scavenging of a catalyst with dilution oxygen occasion air out of the spot.

[0024]

[Example]

[Example 1] (comparative example)

The catalyst for particle state CoMo type hydrodesulfurization 1.2 mm in diameter containing 19.0 % of the weight of  $\text{MoO}_3$  and 4.3 % of the weight of  $\text{CoO(s)}$  was used. Next, at continuing various examples, it is a catalyst (A) about this catalyst. Sulfuration [ it called and / or ] with the sulfur content equivalent to the stoichiometrical theoretical value of sulfide  $\text{MoS}_2$  and sulfide  $\text{Co}_9\text{S}_8$ . [ reserve ] Under [ 100% of the amount of chemicals theories is equivalent to 10.25% of the weight of the sulfur displayed with the dry value which amended heat loss (perte au feu) ].

[0025]This catalyst (A), (1000g), the tert-nonyl polysulfide containing 37 % of the weight of sulfur, and a white spirit type solvent were mixed, and pore volume (550 ml) was filled. Subsequently the catalyst with which it was impregnated was neglected at 150 ° in the low-temperature rotation tank for 2 hours for 1 hour, hydrocarbon was evaporated, and sulfur of organic polysulfide was fixed. Thus, catalyst (B) It obtained. This catalyst (B) The characteristic was indicated to the table.

[0026][Example 2] (comparative example)

About a catalyst (A) and (1000g), it is a sulfur element (S). It was impregnated by the suspension of 105 g, the oleum rapae 22g, and 330 ml of white spirit, subsequently was neglected at low temperature for 1 hour, and heated at 180 ° for 2 hours. Thus, catalyst (C) It obtained.

[0027][Example 3] (comparative example)

About a catalyst (A) and (1000g), it is a sulfur element (S). It was impregnated by the suspension of 105 g, and 55 ml of white spirit, subsequently was neglected at low temperature for 1 hour, and heated at 180 ° for 2 hours. Thus, catalyst (D) It obtained.

[0028][Example 4] The catalyst (B) prepared according to the statement of a precedence example, (C), and (D) It was activated under hydrogen in the cylindrical shape rotary furnace on the following conditions. Namely, temperature:400 °, time:6 hours, a gas: The ratios of hydrogen/nitrogen are 5/95 of mixtures, and pressure:ordinary pressure. At the time of the end

of an activation period, the device was cooled, and under nitrogen, it purged for 4 hours and, subsequently scavenged with air with the mixture of 5% of oxygen in nitrogen by the mixture of 1% of oxygen in nitrogen for 2 hours for 2 hours for 2 hours. a catalyst (E), (F), and (G) -- each, a catalyst (B), (C), and (D) from -- it prepared.

[0029][Example 5] It is a catalyst (B) except not carrying out oxidation passivation, although purged with nitrogen after the end of an activation process. It processed like Example 4. It put in in the flask which avoided air and fulfilled this catalyst by white spirit directly. Thus, catalyst (H) It obtained.

[0030][Example 6] Catalyst [ sulfuration / catalyst ] (A) - (H) It characterized by various methods. Namely, differential thermal analysis (.) under measurement of a carbon content, measurement of a sulfur content, measurement of the heat loss in 500 \*\*, 1 bar of hydrogen, and 5 \*\* the rate of temperature rise for / Or analysis by a differential scanning calorimeter (Differential Scanning Calorimetry-DSC) and X-ray photoelectron spectroscopy, the catalyst test of hydrodesulfurization (hydrodesulfurization) of a gas oil.

[0031]:brewing raw material whose conditions in this test are as follows: The ordinary pressure gas oil and sulfur (S) an initial boiling point - whose end point are 220-370 \*\* respectively Content: 0.8 % of the weight and nitrogen (N) Content: 120 weight ppm. Pressure: 40 bars. Catalyst amount: 70 ml. The amount of brewing material flow : 140ml/hour Temperature: 340 \*\*. The start method includes the stage of 2 hours, and the rise to 340 \*\* at 320 \*\* with pouring of the fluid brewing raw material for a test at the rise to 320 \*\*, and 100 \*\* by 100 \*\*/hour in speed.

[0032]The characterized result was shown in the following abstract table, and notes were attached.

[0033]Catalyst (B) And (C) Since it did not agree in this invention, the reserve sulfurizing method similar to the reserve sulfurizing method by which the application for patent was carried out in United States patent USP 4530917, USP 4719195, and the France patent application 92/04051 was used. "Preliminary sulfuration" of the catalyst was carried out, and the oxysulfide type metallic phase was formed. As a result, the color of these catalysts changed from blue to dark gray. Though a substantial change was accepted to the spectrum of a new article catalyst on the other hand, the SPX spectrum proved that the oxidation number of molybdenum is still +6 mainly. Catalyst (B) And the catalytic activity of (C) was similar.

[0034]Catalyst (D) Were only sulfuration with sulfur and it was still blue. This catalyst became an antecedent basis of the important constant temperature line in DSC under hydrogen, and showed weak catalytic activity.

[0035]Catalyst (E) (F) And (G) It had agreed in this invention, and it is black and the exothermic signal in DSC was not shown at all under hydrogen (since this catalyst is under hydrogen and was already activated by the method of this invention, this is accordant to logic). This catalyst showed the SPX spectrum which is the feature of  $\text{MoS}_2$  of the oxidation number+4. Catalytic activity went up more remarkably than what was measured about the catalyst prepared by the method of the advanced technology.

[0036]Catalyst (H) Catalyst (E) Although it was a homolog, oxidation passivation was not

received, and it is clearly black and had the feature of  $\text{Mo}^{4+}$ . Nevertheless, the catalytic activity of this catalyst is a homolog (H). It is slightly weaker than activity.

The importance of the passivation means which exists in the middle was proved.

[0037][Table]

	A	B	C	D	E	F	G	H
硫黄 (重量%)	/	8.49	8.41	9.31	7.7	8.0	7.9	7.0
熱損失 (重量%)	/	18.0	20.3	9.2	17.8	19.1	12.6	27.1
化学量論 (%)	/	101	103	100	92	96	88	94
炭素 (重量%)	/	8.2	12.0	0.1	5.8	7.9	0.1	/
色	青色	濃灰色	濃灰色	青色	黒色	黒色	黒色	黒色
DSC*	/	+	+	+	-	-	-	/
SPX**	$\text{Mo}^{6+}$	$\text{Mo}^{6+}, \text{Mo}^{5+}$			$\text{Mo}^{4+}$	$\text{Mo}^{4+}$		$\text{Mo}^{4+}$
HDS (%)***	/	100	105	71	115	112	107	104

\*DSC : + は、発熱のピークが温度200～300℃で観測されることを意味する。

— は、この領域でも、他においても50～350℃の範囲全体では、ピークが全く検出されないことを意味する。

\*\*SPX :  $\text{Mo}^{6+}$  は、モリブデンが本質的には酸化数+6であることを意味する。

$\text{Mo}^{6+}$  > 50% は、モリブデンが50%以上において酸化数+6であることを意味する。

$\text{Mo}^{4+}$  は、モリブデンが本質的には酸化数+4であることを意味する。

\*\*\*HDS : 触媒(C)～(H)の水素化脱硫での活性度は、触媒(B)の活性度(活性度=3.66、HDS=95.4%)を参照して計算された。

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[Translation done.]